The Nature of Absolute Zero Temperature

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Abstract

Absolute zero, or zero Kelvin, is presumably the lowest limit of the thermodynamic temperature scale. The theoretical value is determined by extrapolating the ideal gas law; by international agreement, absolute zero is taken as *-273.15* degrees on the Celsius scale. Due to the common misconception that temperature represents the average kinetic energy of particles in substances, the physical nature of absolute zero is not fully understood. Rather, temperature is a measure of the average potential energy associated with various forms of Coulomb force between particles in substances. The lowest potential energy is at the ground state. So, the absolute zero temperature occurs in substances where electrons are at their lowest orbitals and the distances between particles in bonds are at the minimum. At equilibrium, the kinetic energy is also minimized, though it does not necessarily reach zero. For instance, electrons continue to exhibit orbital motion and spinning.

Introduction

The concept of an absolute minimum temperature can be traced back to 1665 in Robert Boyle's work, "New Experiments and Observations Touching Cold".[1] This temperature was initially predicted through Charles's law of volume, which states that the volume of gases tends to expand when heated and is proportional to temperature.[2-3] According to this law, the volume of gases would theoretically reach zero at a temperature of around *-273.15 °C*, commonly regarded as the lowest possible temperature and defined as absolute zero temperature, i.e., *0 K*. However, the physical nature of this minimal temperature is not well understood. It is often assumed that at absolute zero, the fundamental particles of nature exhibit minimal vibrational motion. Nevertheless, this notion is a misconception, as temperature is a measure of potential energy and is not directly linked to the kinetic energy of particle motion.[4] This article seeks to clarify the physics at absolute zero.

Missing Energy in Specific Heat of Gases

Specific heat is the energy needed to raise a unit temperature per unit mass for a given substance. If the temperature could fully represent the kinetic energy of a system, the change in temperature and kinetic energy should be correlated via specific heat. Then, it should be expected that the specific heat energy is utilized to increase the kinetic energy of a system. This relation should be verifiable using the kinetic theory of gases.[5-6] The isochoric molar specific heat for ideal gases predicted in the kinetic theory is

(1) $\qquad C_k = \frac{3}{2}R$

where R donates the molar gas constant (*8.31446261815324*). When compared with the measurements of specific heat for a number of ideal gases, the theoretical values C_k closely match the measurements for the gases with monatomic molecules, exhibiting a *99%* predicting accuracy of the theory. However, it fails to predict the specific heat for gases with polyatomic molecules. The predicted values for polyatomic gases consistently fall short of measurements. The larger the molecules, the greater the prediction error. For instance, the predicted specific heat for octane is only *7%* of the measured value, indicating a *93%* prediction error. In other words, only *7%* of the specific heat energy is allocated to increase the kinetic energy for molecule motion. Where does the majority of specific heat energy go?

To account for the uncalculated energy in the theory, additional terms were introduced, namely vibrational energy for the vibration of particles and rotational energy for the rotation of particles. The energy predicted in the kinetic theory was assumed to account only for the transitional energy of particle motion. The rest of the energy was attributed to the vibration and rotation of particles. Maxwell proposed an equipartition for the energy among the three components,[7] which still cannot justify the miscounted energy. Boltzmann improved the law of equipartition by introducing the concept of degrees of freedom, suggesting that a gas's energy is equally distributed among all of its degrees of freedom.[8-10] Essentially, these adjustments proportionally scale up the transitional energy by the number of freedom degrees. However, this scaleup still cannot justify the surplus of measurements in molar-specific heat that increases along with the size of gas molecules, as indicated in Figure 1.
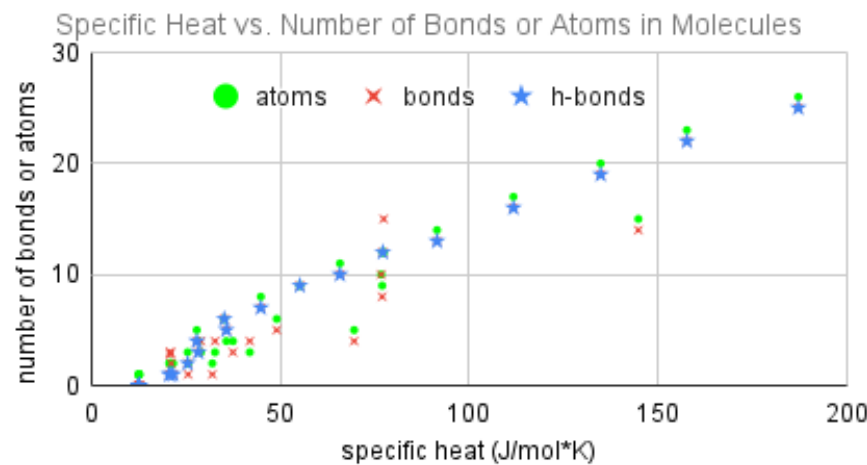

Figure 1, The correlation between the measured isochoric specific heat and the size of gas molecules. The values in the horizontal direction are the measured molar-specific heat and values in the vertical direction are the number of atoms or bonds in gas molecules. The blue stars represent the h-bonds related to hydrogen atoms, while the red crosses donate the other bonds. The coefficient of determination (R^2) of a linear fitting for h-bonds is *0.98*.

Numerous explanations for the equipartition's failure have been proposed. Boltzmann suggested that the gases might not be in thermal equilibrium.[11] Planck and Einstein argued for the existence of a zero-point harmonic oscillator.[12-13] Kelvin finally realized that the assumption of equipartition might be incorrect.[14-17] To account for the size of gas molecules, the number of freedom degrees was replaced by the number of atoms in gas molecules. Hence, Equation (1) is scaled up to

(2) $C_k = \frac{3n}{2} R$

where n donates the number of atoms in gas molecules. To better fit the measured specific heat, the equation is further adjusted in Mayhew's work:[18]

(3) $C_k = \frac{2n+1}{2} R.$

All these modifications did not solve the root problem due to the misconception of temperature representation. If all the specific heat energy were allocated to raise the kinetic energy of a system, should one expect the specific heat of a gas to be greater than that of the liquid because the motion of molecules in liquid is restricted by bonds and therefore liquid accommodates less kinetic energy?

Name	Molecule	Mass	Liquid (kJ/kg*K)	Gas (kJ/kg*K)	Liquid/Gas
Ether	$(C_2H_5)_2O$	74.24	2.21	2.01	1.10
Ethanol	C_2H_5OH	46.07	2.3	1.88	1.22
Propane	C_3H_8	44.1	2.4	1.67	1.44
Acetone	$(CH_3)_2CO$	58.08	2.15	1.47	1.46
Carbon Disulfide	CS_2	76.13	0.992	0.67	1.48
Benzne	C_6H_6	78.11	1.8	1.09	1.65
Chloroform	$CHCl_3$	126.37	1.05	0.63	1.67
Bromine	Br_2	159.8	0.47	0.25	1.88
Propene	C_3H_6	42.08	2.85	1.5	1.90
Ammonia	NH_3	17.03	4.6	2.19	2.10
Water	H_2O	18.02	4.19	1.411	2.97

Table 1, A comparison of isobaric specific heat (C_p) between liquids and gases. The specific heat of liquids and gases is from The Engineering ToolBox.

Table 1 presents specific heats for various substances in both liquid and gaseous states. Contrary to expectations, the substances listed consistently show higher specific heat capacities in their liquid states. Notably, water's specific heat is nearly three times of steam. This raises intriguing questions: Is there a flaw in assuming that all specific heat is allocated to kinetic energy? Is there evidence supporting the idea that temperature represents the average kinetic energy of a system? What precisely does the measurement of temperature entail?

Measurement for Temperature

An electron in an atom tends to retreat to a lower orbital whenever there are electron holes in lower orbitals. During the transition, it releases the potential energy stored at higher orbitals by emitting electromagnetic waves. At a larger bonding distance, the shared electrons involved in a bond are also in higher orbitals. As bonding distance reduces, the bonding electrons also retreat to lower orbitals and radiate the energy, and so does the bond. The perfect blackbody radiation is described in Planck's law.[19-21] By integrating Planck's equation over the frequency, then over the solid angle we found that the power P emitted by a blackbody is directly proportional to the fourth power of its absolute temperature T, known as the Stefan-Boltzmann law:

(4) $P = pT^4$

where P donates the power emitted per unit area of the surface of a blackbody and p represents the Stefan-Boltzmann constant.[22-23] Equation (4) presents the theoretical base for many devices designed for measuring temperature. When using an infrared thermometer to gauge temperature, what the device detects is the average radiation level of electromagnetic waves emitted by a target object, without the need for physical contact. The radiation level corresponds to the potential energy of the target. So, the thermometer measures the average potential energy of a system.

Mercury and alcohol thermometers are also based on the same principle. As the mercury in a thermometer absorbs the radiation energy from its surroundings, its potential energy rises, causing thermal expansion and increasing the length of the mercury bar in the thermometer. Traditionally, the freezing point of water is set at 0 °C under standard Earth pressure, while its boiling point is established at 100 °C. The length of the mercury bar is typically calibrated on a scale for temperature readings. Hence, these thermometers also gauge the average level of potential energy. Is there any thermometer that can directly detect the average kinetic energy?

If the thermometers measure the average potential energy level, it raises the question of how temperature can accurately represent the average kinetic energy of a system. One could argue that the connection becomes apparent through observations of Brownian motion. This might be the source of the misconception about temperature. Estimations indicate that the random motion of molecules does not have sufficient momentum to drive Brownian motion. Instead, the particles in Brownian motion are predominantly propelled by transimpacts.[24] A transimpact is an interaction between particles during an atomic electron transition. As an electron jumps to a higher orbital, the size of the electron cloud expands, increasing the volume of the atom and molecule. The spacing between adjacent particles is reduced, resulting in repulsion to adjacent particles via electrostatic force and thereby kicking them apart. Thus, Brownian motion correlates with potential energy rather than the kinetic energy of molecule motion.

Therefore, temperature should reflect the potential energy of a system rather than its kinetic energy. With this understanding, the correlation between the number of bonds in gas molecules and the unexplained specific heat in the kinetic theory becomes more comprehensible. In the case of monatomic gases, the specific heat is primarily ascribed to the kinetic energy for the motion of gas molecules, enabling the kinetic theory to make precise predictions for the specific heat. For polyatomic gases, the surplus energy in the kinetic theory is designated to elevate the potential energy of the bonds. This energy is employed to disperse the particles, increasing the potential energy of the bonds. Increased potential energy corresponds to elevated radiation levels of electromagnetic waves, resulting in higher temperature according to Equation (4).

When energy is introduced into a system, potential components absorb it directly, while transimpacts also convert a portion into kinetic energy. Over time, the system will attain a dynamic equilibrium between potential energy and kinetic energy. When the influx of energy diminishes, the system will emit more energy than it receives, leading to a net reduction in potential energy and a loss of equilibrium. Consequently, impactrans, the reverse mechanism of transimpact, will transform kinetic energy into potential energy to restore equilibrium.[25] In either scenario, changes in potential energy take the lead, while kinetic energy follows suit. The temperature rises and falls along with the change in the potential energy of a system. The equilibrium process gives rise to an illusion of a direct correlation between temperature and kinetic energy. However, in reality, this entails an indirect and secondary relationship, which leads some to mistakenly believe that temperature directly corresponds to kinetic energy.

The Energy Represented by Temperature

There is no question that temperature signifies a certain degree of internal energy within a substance. The question is to what extent temperature can represent the total energy within a body. Energy can be stored in two primary forms: kinetic energy and potential energy. Kinetic energy is associated with the motion of objects, while potential energy is retained between objects at a specific distance from each other. Both forms of energy are associated with a field of force. By definition, energy is the work done by a force on an object over a distance:

$$(5) \quad d_E = Fd_s$$

where d_E denotes the object's energy increment by a force F after moving a distance d_s in the direction of the force. For example, when the velocity of a resting object is accelerated by a force to v, the object's kinetic energy can be evaluated by integrating Equation (5):

$$(6) \quad K = \int_0^v d_E = \int_0^v Fd_s = \int_0^v mad_s = \int_0^v m\frac{d_v}{d_t}d_s = \int_0^v md_v\frac{d_s}{d_t} = \frac{1}{2}\int_0^v md_{v^2} = \frac{1}{2}mv^2$$

where K denotes the kinetic energy, m represents the object's mass, a indicates the acceleration, and v is the velocity of the object. Equation (6) represents the classical form of kinetic energy, indicating that kinetic energy exists in any moving body. Similarly, the kinetic energy of a rotational object can also be computed from Equation (5). Essentially, there is kinetic energy for any moving particle, such as the moving, vibrating, or spinning of an orbiting electron.

When work is done to an object against a force, its potential energy increases, which can also be evaluated using Equation (5). For instance, an object is raised against gravity on Earth. Its increment in potential energy can be calculated by integrating the gravitational force over the elevated height:

$$(7) \quad U = \int_0^h d_E = \int_0^h Fd_s = \int_0^h mgd_s = mg(h - 0) = mgh,$$

where U denotes the increment of the potential energy of the object, m represents the object's mass, g refers to the acceleration due to the gravitational force, and h stands for the elevated height of the object. For simplicity in the above evaluation, the gravitational acceleration g is assumed to be a constant for a small elevation on Earth. For a more accurate calculation, Newton's universal gravitation law can be used for the force in the evaluation above. Expression (7) represents a simple form of potential energy increment when an object is pulled away from its attraction source. Potential energy exists in any object in a field of force. Essentially, whenever an object is pushed away against the field of force, its potential energy is increased. As the bonding distance between atoms or molecules is extended, its potential energy is also raised by the work used to stretch the bonding distance. When a bonding distance extends, the electrons involved in the bond have to move at higher orbitals and therefore also possess higher potential energy.

To understand what energy component in a body of substance that temperature represents, let's explore the constituents of energy in substances. According to Einstein's mass-energy equation:

(8) $E = mc^2 = K + m_0 c^2$

where E donates the total energy in a body of substances, such as an object or a gas system, m represents the relativistic mass of the object, m_0 refers to the rest mass, c is the speed of light, K stands for the kinetic energy appreciation due to the increase in the object's speed.[26-27] Note that there is still internal energy in the object regardless of its motion. For instance, through a series of nuclear fusions, a body of helium turns into iron. Its mass reduces from m_0 to m_f, where m_f represents the mass of iron. The released nuclear energy, also potential energy between nucleons in helium, is proportional to the mass deficit, $(m_0 - m_f)c^2$. Furthermore, there is still potential energy in the bonds between iron molecules and kinetic energy due to the motion of the particles. This portion of the energy is $(m_f - m_g)c^2$, where m_g donates the iron mass at the ground state. Hence, the total energy of a body given in Equation (8) can be reformulated as

(9) $E = E_a + m_g c^2$

where E_a denotes the total accessible energy in today's technologies, representing the sum of kinetic energy and potential energy in a body:

(10) $E_a = K_a + U_a$

where K_a refers to the total kinetic energy due to the motion of the body and particles in the body and U_a donates the total potential energy of the body. As demonstrated earlier, the energy represented by temperature is potential energy. The total accessible potential energy in a body is the sum of the potential energy of particles in different fields of force:

(11) $U_a = U_s + U_c + U_g$.

where U_s denotes the potential energy arising from strong force between nucleons, U_c represents the potential energy associated with Coulomb force between particles, and U_g refers to the potential energy resulting from gravitational attraction between particles. Nuclear energy is multiple orders of magnitude greater than the potential energy due to the Coulomb force. However, it is only accessible via nuclear reactions. On the other hand, the potential energy associated with gravitational force is 36 orders of magnitude less than potential energy due to Coulomb force. For a system that undergoes nuclear reactions, such as the Sun, temperature represents primarily the nuclear energy (U_s) while other components are negligible. For a system without nuclear activities, temperature measures primarily the potential energy of bonds (U_c) where U_g is negligible.

Among the three distinct components of potential energy, the energy associated with the Coulomb force (U_c) is the most active constituent in thermodynamic processes on Earth. Historically, this portion of the energy is typically indicated by the measurements of temperature. However, it again consists of three components, resulting from three manifestations of Coulomb force:

(12) $U_c = U_e + U_m + U_i$.

where U_e donates the potential energy due to the attraction between electrons and their host nuclei, U_m represents the potential energy associated with the bonds between atoms within individual molecules, and U_i refers to the potential

energy resulting from the bonds between molecules. The attraction between an electron and its host nucleus can also be viewed as a form of bond. The potential energy of a bond increases at a larger bonding distance. All these bonds may resemble capacitors with varying capacitances, each signifying distinct capacities for energy storage. The capacity of these components varies between different substances and in different states, and so does their significance to the change in temperature.

Since the mass of an electron is three orders of magnitude less than a neutron, the capacity of U_e is much smaller than the other two components. Because the intermolecular bonds are already broken in gases, molecules move freely without the restriction of the bonds, and thereby U_i is negligible. In monatomic gases, there is also no molecular bond, i.e., $U_m = 0$. Therefore, K_i becomes prominent and represents primarily energy storage. This characteristic allows the kinetic theory to make accurate predictions in specific heat for ideal gases with single-atom molecules, as the majority of energy is dedicated to increasing the kinetic energy associated with particle motion. In polyatomic gases, U_m emerges as another major component for energy storage, evident in the correlation between the number of bonds and the unaccounted energy in kinetic theory, as shown in Figure 1.

In liquid and solid, molecules are constrained by intermolecular bonds. Consequently, K_i is negligible, while U_i becomes more pronounced. This explains why the specific heat of liquid and solid is usually greater than the corresponding gas even though the kinetic energy is negligible. Other forms of energy, such as those resulting from particle vibration and rotation, are relatively less significant compared to the potential energy of bonds due to their smaller storage capacities. Overall, potential energy related to the Coulomb force represents a small portion of the total accessible energy of a body. However, it is the most active constituent of energy for many physical, especially thermodynamic, processes in the environment on Earth. Conventionally, this portion of energy is indicated by the measurement of temperature.

On the other hand, it is not to say that kinetic energy has nothing to do with temperature. The kinetic energy in a system exchanges with potential energy and attains a dynamic equilibrium through interactions of transimpact and impactrans. Any energy alteration in one component will prompt a shift in the equilibrium, leading to the exchange of different forms of energy to restore a new equilibrium. Therefore, kinetic energy is indirectly linked to the temperature.

The Physics at Absolute Zero Temperature

Electron binding energy, or ionization energy, is the energy required to free an electron from its atomic orbital. This energy depends on the current electron orbital:

$$(13) \quad E_e = - U_e$$

where E_e donates the binding energy of an electron and U_e refers to the electron's potential energy at its current orbital. Note that the potential energy of an electron is conventionally defined as zero as there is no interaction at an infinite distance. Thus, the higher the orbital of an electron, the less binding energy. In other words, it requires less energy to remove an electron from its host atom at a higher orbital. At the ground state, it takes most energy to free an electron. This relation is the same for bonds:

$$(14) \quad E_m = - U_m$$

and

(15) $E_i = -U_i$

where the letter m donates the molecular bond in Equation (14) and i to the intermolecular bond in Equation (15). The larger the distance between bonding particles, the more potential energy in the bond. It requires less energy to break a bond with a larger bonding distance.

Although the storage capacity for energy varies among different bonds, their radiations are at the same level within a substance. This is because a bond with a higher radiation level will emit more electromagnetic waves than it receives, while a bond with lower radiation will absorb more electromagnetic waves. At equilibrium, the radiation levels of these bonds should be equal. Therefore, the radiation level and potential energy of different bonds rise and fall at the same time, which is reflected in the measurement of temperature.

As energy is introduced to a substance, the potential level rises and binding energy reduces. To a certain extent, the binding energy becomes low enough that the bonds cannot hold the particles together against the transimpacts.[25] The intermolecular bonds are typically the weakest and break first, leading to a phase transition.

For instance, as energy increases in a solid, the potential energy rises, and intermolecular bonds weaken while the impact level of transimpacts intensifies. To a certain level, the bonds cannot hold the molecules together against transimpacts. As bonds shatter, the molecules the bonds break apart, leading to a phase transition. The radiation of intermolecular bonds is anchored at the level corresponding to the transimpact intensity beyond which the bonds are broken. The emission level of other components in the solid is synchronized at the same level. This is why phase transition remains at constant temperatures.

During a phase transition, latent heat is partially allocated to break bonds in the amount of binding energy as indicated in Equation (15). The rest of the latent energy is attributed to the increase in the kinetic energy of the molecules that are just liberated from the restriction of bonds. Contrary to traditional belief, the kinetic energy rises during a phase transition. Since each component of energy in a system will eventually attain equilibrium with other components, the kinetic energy must also be limited to a certain proportion with potential energy, while sharing the latent heat during the phase transition.

In the reverse direction, as energy is removed from a system, the potential energy decreases, and so does the temperature. The lowest potential is at the ground state as any transition to a lower energy state becomes impossible. Thus, absolute zero temperature occurs in substances where electrons are at the lowest orbitals and the distance between bonding particles is at the minimum. There is no further transition to a lower energy state. The minimum temperature corresponds to the lowest potential level. Without detectable radiation, the measurements of thermometers should be naturally at the lowest readings in the absence of electromagnetic wave. In equilibrium at absolute zero, kinetic energy is minimized, though it does not necessarily reach zero, as electrons continue to exhibit orbital movement and self-spinning.

Consider a scenario where a system is designed to exclusively emit energy through electromagnetic waves while remaining impervious to external energy input. In this setup, the system's potential energy gradually diminishes to ground level over time. Equilibrium processes, such as transimpact and impactrans, facilitate the reduction of kinetic energy to its minimum level. Any remaining kinetic energy, like particle vibrations, transforms into potential energy through impactrans,

eventually emitted as radiation. Assuming the absence of nuclear activities, such as radiative decay, the system will ultimately approach absolute zero temperature.

Conclusions

Temperature is a measure of the average potential energy of substances. The lowest potential energy is at the ground state. So, the absolute zero temperature occurs at the ground state of substances. At this state, the kinetic energy is also minimized, though it does not necessarily reach zero as electrons are still moving in their orbitals. Thus, the concept of absolute zero temperature primarily relates to the minimum level of energy associated with the Coulomb force.

See Also

- [Unified Theory of Low and High-Temperature Superconductivity](#) [(PDF)](#)
- [Superfluids Are Not Fluids](#) [(PDF)](#)
- [Electron Tunnel](#) [(PDF)](#)
- [LK-99 Limitations and Significances](#) [(PDF)](#) [(中文)](#)
- [The Cause of Brownian Motion](#) [(PDF)](#)
- [The Process Driving Crookes Radiometers](#) [(PDF)](#)
- [Can Temperature Represent Average Kinetic Energy? (PDF)](#)
- [Why Phase Transition Temperature Remains Constant](#) [(PDF)](#)
- [Is Thermal Expansion Due to Particle Vibrating? (PDF)](#)
- [The Nature of Absolute Zero Temperature (PDF)](#)
- [Misconceptions in Thermodynamics](#) [(PDF)](#)
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- [Tidal Energy Is Not Renewable](#) [(PDF)](#)
- [How to Understand Relativity](#) [(PDF)](#)
- [The Simplest Derivation of $E = mc^2$](#) [(PDF)](#)

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